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1.119.546



## PATENT SPECIFICATION

DRAWINGS ATTACHED

1.119.546

Date of Application and filing Complete Specification: 28 Feb., 1966.  
No. 8615/66.

Application made in United States of America (No. 435,796) on 1 March, 1965.

Complete Specification Published: 10 July, 1968.

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Index at acceptance:—D2 W (2, 3A2C, 3A4B, 3A4X, 3B1, 3B6, 7)

Int. Cl.:—D 21 c 3/00

## COMPLETE SPECIFICATION

## Improved method of Treating Fibrous Material

We, THE INSTITUTE OF PAPER CHEMISTRY, a corporation organized and existing under the laws of the State of Wisconsin, of Appleton, State of Wisconsin, United States of America do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates generally to fibrous material which contains a significant amount of carbohydrate and non-carbohydrate materials, and its treatment, and, more particularly, it relates to fibrous material which contains a significant amount of carbohydrate material and native lignin or modified lignin.

Various processes have existed for many years for the treatment of fibrous materials, such as wood, for purposes of preparing a pulp which may be made into a sheet material, as for example, paper. In this connection, treating processes have been evolved which utilize sulphite compounds for the treatment of the fibrous materials and these processes have been carried out under acid or near-neutral conditions. These processes are known as the sulphite, bi-sulphite, and neutral sulphite process. In addition to the sulphite compounds, the previously known processes have used sulphate compounds and have also utilized caustic soda for preparing pulp and these processes are known as the sulphate or kraft process, and soda process, respectively. In all of these processes, lignins are converted to soluble or removable compounds and, in the case of the use of the sulphite compounds, the lignin is converted into lignosulfonates and in the case of the soda or kraft process, it is converted into alkali lignin having additional hydroxyl groups. It is important to note that in each case, the phenolic rings of

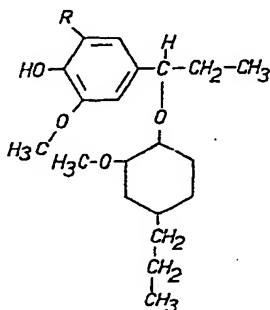
the lignin structure appear to remain intact. It is also important to note that in the various known commercial processes for treating fibrous materials by chemical action, more carbohydrate materials, on a weight basis, are removed from the fibrous material by the treating chemicals than lignin materials. When acid treatment is used, i.e., treatment with the sulphite compounds, the carbohydrate materials hydrolyze to sugars and this is especially the case in respect to hemicelluloses. On the other hand, alkaline treatment which results from the use of the sulphate or caustic soda, tends to break down the carbohydrate materials into simple acids and removes acetyl groups in the hemicelluloses. Because of these treatments, the sulphite pulps tend to be soft and weak, and the kraft or soda pulps tend to provide a strong but hard pulp.

This invention is directed to any fibrous material which for purposes of this specification is defined as that material which contains a significant amount of both carbohydrate and non-carbohydrate material, whether or not the material has been previously processed. The non-carbohydrate material in the fibrous material contemplated comprises a significant amount of native lignin or modified lignin. Accordingly, the term "fibrous material", as used herein, will refer to any material within this definition and, obviously, the fibrous material includes wood, ground wood, newsprint, waste paper, bast and flax. However, this invention is not directed, nor particularly related, to such fibrous materials as cotton, rags, or linters.

The term "native lignin" refers to those materials which are believed to have the following general formula and which exist in wood or other raw material in native form:

[Price]

Price



wherein R is H or  $\text{OCH}_3$ .

Modified lignin, as used herein refers to those materials which have been chemically treated to facilitate removal of them from fibrous material as is done by the sulphite, soda and kraft processes.

It is known that wood generally comprises the following:

(a) Carbohydrate Materials	60—80%
Cellulose	40—55%
Hemicellulose	15—25%
(b) Non-Carbohydrate Materials	20—40%
Lignin	15—30%
Extractives	3—10%

The foregoing chemical treating processes for fibrous material effect removal of lignin but, in so doing, the carbohydrates are also removed. As a result, when most lignin is taken out of the fibrous material, the yield is only about fifty percent of the wood.

The chemical treating processes for fibrous materials are necessarily carried out at high temperature in an aqueous solution with resulting high pressure. This not only requires high equipment costs with associated maintenance and safety problems, but, perhaps, more significantly, it effects accelerated degradation of cellulose and hemicellulose. In the sulphite processes, the fibers are weakened, while in the kraft process, the degradation of cellulose is less severe, but most of the hemicelluloses are lost in the form of organic acids. These by-products of the chemical treating processes can result in stream pollution.

The commercially used chemical treating processes for fibrous materials cause the production of coloured bodies and this is particularly the case in the case of alkaline treatments. As a result, bleaching is often necessary and this bleaching causes further degradation of the pulp.

Furthermore, the chemical treating processes for fibrous materials have provided by-products which have only been partially converted to useful products. In this connection, the sugars in the spent liquor from the sulphite processes may be fermented into alcohols or yeast, whereas the lignosulfonates, resulting from the processes, may be used for a variety of purposes. However, other by-products re-

main in the spent liquor. On the other hand, if the organic materials in the spent liquor from the sulphite processes are burned and inorganics are recovered, there are added cost burdens involved. The by-products of the kraft process are conventionally burned to provide heat and recover pulping chemicals. While this is an economical process, volatile sulphur compounds may cause pollution problems.

It has been known that wood may be treated with oxidizing chemicals to selectively remove lignin and provide a lignin-free material which has been identified by The Institute of Paper Chemistry as "holopulp". The holopulp contains both celluloses and other carbohydrate materials particularly the hemicelluloses. However, these known procedures for oxidizing lignin have not been carried out on a commercial scale and, to our knowledge, have only been carried out on a laboratory basis. Furthermore, these known processes have not provided a pulp which has most desired properties for paper making. In addition, these processes have not been considered satisfactory for commercial purposes because they have required long times for treatment and have been generally uneconomical.

According to the invention there is provided a method of treating fibrous material containing lignin and carbohydrate materials to remove the lignin from the fibrous material without substantial removal of the carbohydrate material in which the fibrous material is reacted with a delignifying agent and the fibrous material is separated from the lignin characterized by contacting the fibrous material with chlorine dioxide or a compound which yields chlorine dioxide upon decomposition, peracetic acid, performic acid, or perpropionic acid, maintaining the pH between 2.5 and 4.0 during the reaction and terminating the reaction before the residual lignin content of the fibrous material is reduced to below 2.0 per cent by weight.

All percentages set forth herein are by weight.

The present invention is particularly directed to providing a commercial process for selective delignification by oxidative reactions. The broad concept of delignifying certain fibrous materials is disclosed in United States Letters Patent No. 2,939,813. However, the process of that patent requires the use of large amounts of peracetic acid for the oxidation reaction and also discloses yields of less than about 60 percent. It is not believed that that patent provides a process which is adequate for commercial purposes.

Specific embodiments of the invention will now be described by way of example with reference to the accompanying drawings in which;

Figure 1 is a graph illustrating the time of delignification of different sized fibrous mater-

ials. Plotted on the axis of ordinates is the present lignin, on a log scale, and plotted on the axis of abscissas is the time of treatment;

5 Figure 2 is also a graph illustrating the effect of mild alkaline pretreatment on time for delignification, the axes of ordinates and abscissas being the same as in Figure 1;

10 Figure 3 is a triangular diagram illustrating the substantial removal of carbohydrate material when delignification by oxidation is carried on to effect removal of lignin to below about 2 percent of the fibrous material. The graph further shows the effect of different mild alkaline treatments; and

15 Figure 4 is a graph showing the sharp rise in consumption of chlorine dioxide when more than about 16 percent lignin is removed, i.e., the level of lignin in the wood is less than about 2 percent. The graph is plotted with chlorine dioxide consumption along the axis of ordinates and the percent of lignin removed along the axis of abscissas.

20 The graphs of Figures 1 to 4 were obtained from fibrous material having a lignin content of approximately 18 percent by weight. Similar results are obtained from fibrous materials having higher or lower lignin contents.

30 In accord with the present invention, fibrous material, which may be derived from raw material, such as wood, straw, or grasses, or derived from previously treated fibrous material, such as pulp board, waste paper, or newsprint, is lacerated to permit more rapid chemical reaction. The lacerated fibrous material may then be extracted to remove hydrophobic material, such as tars, oils and inks. The extracted, lacerated fibrous material may then be subjected to a mild alkaline pre-treatment. We have found that differential squeezing of the pre-treated fibrous materials without fiber damage provides more rapid treatment in the next step of the process.

45 The fibrous material is then subjected to selective delignification by means of an oxidant selected from chlorine dioxide and compounds which provide chlorine dioxide, such as sodium chlorite and sodium chlorate, peracetic acid, performic acid and perpropionic acid under particular conditions, to be hereinafter pointed out. The selective delignification of this invention is only carried out until the residual native or modified lignin is at a level of between 2 percent and 5 percent. Less carbohydrate materials should be removed overall from the fibrous material than lignin materials during the pre-treatment and selective de-lignification.

60 We have found that by maintaining at least 2 percent of the lignin in the fibrous material, the amount of carbohydrates retained in the fibrous material is maximized and a satisfactory pulp is provided.

65 After selective delignification of the fibrous material, the resulting pulp is defibered and,

in this connection, defibering may be effected by mechanical action alone through the use of beaters or refiners, and may be combined with a mild alkaline treatment.

70 The pulp yield from the process of this invention is in excess of 60 percent and, desirably, will be in excess of 70 percent of the initial fibrous material.

75 The size of fibrous particles treated in accord with this invention is significant to provide rapid chemical reaction. A comparison of various sized materials for treatment is shown in Figure 1 of the drawings in which the extent of delignification of Aspen wood, at 72 degrees C., is shown as a function of time of treatment for chips, wafers and shreds. 80 The various particles were sized, as follows:

Form	Length	Width	Thickness
Chips	5/8"	1"	1/8"
Shreds	1/2"	1/8"	1/32"
Wafers	2"	1/2"	1/32" (or less)

85 It is obvious that much more rapid delignification can be carried out with the smaller sized particles, specifically the shreds.

90 In Figure 2 there is shown a graph illustrating the effect upon delignification of Aspen wood with alkaline pre-treatment with 0.1 N to 0.5 N sodium hydroxide. The pre-treatment was effected at 50 degrees C. for about 40 minutes at atmospheric pressure after wetting the wood at 25 degrees C. under vacuum for about 20 minutes. When delignification is carried out at 70 degrees C., it is apparent that the use of mild alkali pre-treatment expedites the delignification, but, at the same time, there is some loss of carbohydrate materials when this pre-treatment is employed. In this connection, the use of 0.1 N sodium hydroxide effects about 5 percent carbohydrate removal, whereas 0.5 N sodium hydroxide effects about 7 percent carbohydrate removal. Higher concentrations of sodium hydroxide are not desired because of the undue loss of yield. Furthermore, as will appear more clearly hereinafter, the reduction in carbohydrates in the pre-treatment step appears to effect higher losses of carbohydrates during the delignification step. Other pre-treatments may be utilized. 110

115 After pre-treatment, the fibrous material is differentially squeezed and washed. Differential squeezing comprises pressing the fibrous material while effecting relative fiber movement without significant fiber damage. This can be effected by squeezing the fibrous material between surfaces moving at different speeds.

120 We have found that for most efficient processing, chlorine dioxide is desirably used as the oxidizing agent. Of course, chlorine dioxide can be provided from compounds, such as sodium chlorite and sodium chlorate which decompose to yield chlorine dioxide under 125

acid and reducing conditions. However, the use of the gas has several advantages in commercial practice and is more economical to use. Whereas peracetic, performic and propionic acids may be utilized, they are higher in cost than chlorine dioxide and are half as effective inasmuch as they only provide one oxygen per mol for oxidation, whereas chlorine dioxide provides two oxygens per mol for oxidation.

Accordingly, chlorine dioxide is preferably dissolved in an aqueous solution and is circulated through the fibrous material. Chlorine dioxide, under certain partial pressure conditions, however, is quite explosive and, accordingly, the chlorine dioxide gas should not be released under such certain conditions.

As before pointed out, the delignification of the fibrous material should be carried out until 2 percent or more lignin remains in the fibrous material. As above indicated, alkaline pre-treatment effects initial removal of carbohydrate before selective delignification. In Figure 3, which is a triangular diagram, the effects of removing lignin below about 2 percent are illustrated. It will be seen that at below about 2 percent lignin content, there is a very substantial removal of carbohydrates in the delignification process, regardless of the pre-treatment. However, it will be apparent that as the extent of the pre-treatment increases, the amount of carbohydrate removal increases.

In Figure 4, the consumption of chlorine dioxide in percent of fibrous material is shown as a function of the percent of lignin removed from the fibrous material. It will be seen that there is a sharp increase in the required chlorine dioxide, when the lignin removed exceeds 16 percent, i.e., when the lignin remaining is less than 2 percent.

The temperature of the delignification reaction should be maintained between 40 degrees C. and 75 degrees C. At lower temperatures, unusually long times are required for delignification, whereas at higher temperatures, the chlorine dioxide has low solubility and tends to provide difficulties in handling. With the other oxidants, there is degradation of the fibrous materials and decomposition of the oxidants at the higher temperatures.

The aqueous solution must be maintained at a pH within the range of 2.5 to 4 and this can be controlled by suitable addition of base. At lower pH values, excessive hydrolysis of the carbohydrates occurs and the selectivity of delignification is lost. If the pH of the aqueous solution is not controlled, the pH falls to about 1. At pH values above about 4, the chlorine dioxide is not readily available for delignification.

The aqueous solution should be saturated with chlorine dioxide to provide a level of 4 to 5 grams of chlorine dioxide per liter of aqueous solution. By maintaining this level of

chlorine dioxide in the aqueous solution, we have been able to remove about one part by weight of lignin with a consumption of about one part by weight of chlorine dioxide in relatively short periods of time. This is significantly better than those previously known and with the process of the invention an economical and feasible commercial process is provided.

The delignified material is then desirably defibered through the use of mild alkali solutions. The use of strong alkaline solutions results in the loss of carbohydrate material and reduction in yield. However, the use of the alkaline solutions appears to attack the wall between mother-daughter cells in wood products, whereas radial cell walls appear to break under mechanical action. Accordingly, alkaline fiberizing of the delignified pulp is desired.

Fibrous materials having less than about 2 percent lignin may be desired and, in such event, a two-stage process is contemplated, wherein the fibrous material is treated to remove lignin down to about 2 percent and the residual lignin is removed in a second stage by means of the same or another oxidant.

As before indicated, the process of the invention has unique application to used fibrous material which has undergone pulping or other treatment, as for example, newsprint and waste paper. This process appears to improve certain fiber characteristics so that these materials may be processed to provide fibers for re-use without the fiber degradation effected by the re-working of waste paper and newsprint, as done in various jute processes. The process of the invention permits the re-use of fibers in papers of the same or better grade, which is an outstanding advantage of the process.

The following Examples will make more clear the practice of the present invention. "Zero-Span" is the average fiber tensile strength expressed as pounds force per inch of specimen width. "Tear Factor" is the Elmendorf tear, in grams, divided by the basis weight of the specimen in grams per square meter. "Unscreened" means the fibers were not screened.

#### EXAMPLE 1

One hundred pounds of debarked Aspen wood are shredded, are placed into a closed tank, and are immersed in 600 pounds of 0.25 N sodium hydroxide at 25 degrees C. The tank is evacuated to 10 inches of mercury absolute and held under this vacuum for about one-half hour. The tank is then heated to 40 degrees C. to 50 degrees C. in 10 to 30 minutes. Then the shreds are drained. The shreds are passed through press rollers which are moving at different speeds to provide a fiber to fiber shearing action which significantly reduces the time for oxidation. This action is different from defibration and functions to

press and work the fibers without fiber damage. The pressed fibrous material is then washed and ready for selective delignification.

- 15 Chlorine dioxide gas is generated and dissolved in water at about 50 degrees C., the water dissolving the gas to a level of about 4.7 grams per liter. About 1,000 pounds of water containing the gas is used to immerse the shreds and the solution is circulated and gas introduced into the solution to maintain saturation in the solution. As the solution is recirculated, sodium hydroxide is added to

maintain the pH at 3 to 4. The shreds are treated for 3.5 hours and they are drained.

The drained shreds are then immersed in 0.1 N sodium hydroxide and the mixture is fed to a mill for 5 minutes. The solution is drained off and the pulp washed and screened.

The resulting pulp has about 2 percent lignin remaining and a yield, over-all, of 75 percent is provided. After screening, a yield in excess of 60 percent is provided. A comparison with conventional pulps is set forth below:

	Acid Sulfite	Bisulfite	Neutral Sulfite	Kraft	Delignified
Yield, overall	58	60	58	54	75
Yield, screened	58	57	54	47	61
Lignin, % in screened pulp	2.3	4.1	3.3	4.4	2.6
G.E. Brightness, %	60	58	64	28	60
Zero-Span, lb./in.	48	56	68	65	59
Beating time, min. to 300 C.S.F.	16	17	17	25	16
Apparent density, g./cc.	0.79	0.74	0.73	0.78	0.72
Tensile strength, lb./in.	26	33	35	31	34
Tear	0.44	0.64	0.93	0.88	0.69
Opacity, %	72	72	74	90	62

#### EXAMPLE II

- 30 In accord with this Example, shreds of Aspenwood are treated with an aqueous solution comprising about 47 percent peracetic acid, 11 percent hydrogen peroxide, 12 percent acetic acid, the solution having a pH of less than about 1. The ratio of the solution to wood is 7 to 1 and, in accord with the

following Table, sodium acetate, sodium hydroxide and ammonium hydroxide are added to the solution to raise the pH to the indicated level. The initial amount of peracetic acid in the solution comprises 120 percent of the weight of the wood. The selective delignification was carried out at 70 degrees C., with the results set forth in the Table below.

Run	Alkali	pH		Beating time, min. to 300 C.S.F.	Pulp Yield % of Wood	G.E. Brightness, %	Zero-Span Tensile strength Unscreened lb./in.
		Initial	Final				
1	NaAc	3.8	3.5	120	73	82	64
2	NaAc	3.8	3.6	60	76	75	48
3	NaOH	3.8	3.6	60	76	75	49
4	NH <sub>4</sub> OH	3.8	3.6	60	76	76	56
5	NH <sub>4</sub> OH	4.0	3.6	120	70	83	72

It was found that when the pH exceeds about 4, the wood was relatively raw and there is a tendency to decrease the zero-span tensile strength of the fibers. At pH values below about 2.5 undue degradation of the pulp occurs.

### EXAMPLE III

In accord with this Example, shreds of Aspenwood are treated with the same aqueous solution containing peracetic acid as was utilized in the previous Example. The ratio of the solution to wood is 9 to 1 and the pH of the solution is adjusted to 2.7 by the addition of ammonium hydroxide. The aqueous solution is diluted to provide a solution containing peracetic acid at a level of 47 grams per liter and this corresponds to about 42 percent of the weight of the wood. The selective delignification is carried out at 50 degrees C. for 9-1/2 hours. The yield is 85 percent and the residual lignin is 3.9 percent based upon the initial wood. The consumption of peracetic acid is 37 percent of the initial wood and the ratio of peracetic acid used to lignin removed is 2.6 to 1 on a weight basis.

A particular advantage in the use of peracetic acid is that the pulping system may be almost completely confined to carbon, oxygen and hydrogen, without complications of foreign elements such as substantial amounts of sulfur, chlorine or sodium. Furthermore, after the active oxygen is used up, peracetic acid is converted to acetic acid from which addition reagent is made. In addition, peracetic acid is quite soluble in water so that high concentrations may be utilized.

From the foregoing, it will be apparent that commercially feasible processes have been developed for the treatment of fibrous material. The processes provide a hydrodynamically stable pulp which has high initial brightness. The pulp is provided in high yield and the by-product compounds, specifically hololignins, are unique to the paper industry. The pulp has various unique properties.

Furthermore, the process has new and novel applicability to pulp board, waste paper and newsprint, and provides valuable fibers.

### WHAT WE CLAIM IS:—

1. A method of treating fibrous material containing lignin and carbohydrate materials to remove the lignin from the fibrous material without substantial removal of the carbohydrate material in which the fibrous material is reacted with a delignifying agent and the fibrous material is separated from the lignin, characterized by contacting the fibrous mater-

ial with chlorine dioxide or a compound which yields chlorine dioxide upon decomposition, peracetic acid, performic acid, or perpropionic acid, maintaining the pH between 2.5 and 4.0 during the reaction and terminating the reaction before the residual lignin content of the fibrous material is reduced to below 2.0 percent by weight.

2. A method in accordance with claim 1 further characterized by contacting the fibrous material with the compound at a temperature between 40°C. and 75°C.

3. A method in accordance with claim 1 or claim 2 further characterized by lacerating the fibrous material and subjecting the fibrous material to a mild alkaline treatment prior to contacting the fibrous material with the compound.

4. A method in accordance with claim 3 further characterized by pressing the pretreated fibrous materials between surfaces moving at different speeds prior to contacting the pretreated fibrous material with the compound.

5. A method in accordance with claim 4 further characterized by washing the pretreated and pressed fibrous material prior to contacting the pretreated fibrous material with the compound.

6. A method in accordance with any one of claims 1 to 5 further characterized by contacting the separated fibrous material with an additional amount of the compound to remove an additional amount of lignin.

7. A method in accordance with any one of claims 1 to 6 further characterized by defiberizing the separated fibrous material.

8. A method in accordance with claim 7 further characterized by carrying out the defiberizing under mild alkaline conditions.

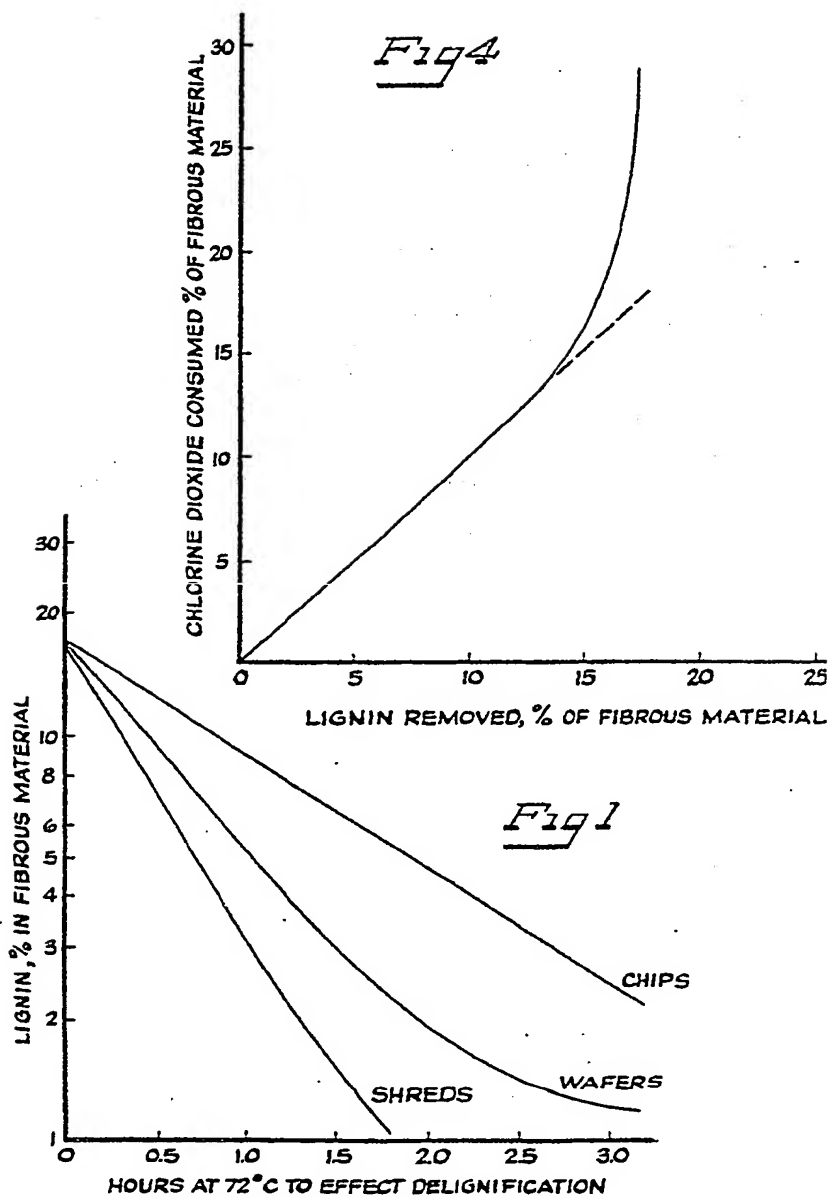
9. A method in accordance with any one of claims 1 to 8 further characterized by employing a solution of chlorine dioxide containing 4 to 5 gms of chlorine dioxide per litre of aqueous solution.

10. A method in accordance with any one of claims 1 to 9 further characterized by preparing the fibrous raw materials in the form of small chips or shreds.

11. A method of treating fibrous material according to claim 1 substantially as herein described with reference to the accompanying drawings.

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COMPLETE SPECIFICATION

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